

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 87107743.4

⑭ Int. Cl.⁴: H01L 21/31, G03F 7/26

⑮ Date of filing: 27.05.87

⑯ Priority: 29.05.86 JP 124123/86

⑰ Date of publication of application:
02.12.87 Bulletin 87/49⑱ Designated Contracting States:
DE FR GB⑲ Date of deferred publication of the search report:
20.07.88 Bulletin 88/29⑴ Applicant: FUJITSU LIMITED
1015, Kamikodanaka Nakahara-ku
Kawasaki-shi Kanagawa 211(JP)⑵ Inventor: Nakamura, Moritaka c/o FUJITSU
LIMITED
Pat. Dep. Kosugi Fujitsu Bldg 1812-10
Shimonumabe
Nakahara-ku Kawasaki-shi Kanagawa 211(JP)⑶ Representative: Greenstreet, Cyril Henry et al
Haseltine Lake & Co. Hazlitt House 28
Southampton Buildings Chancery Lane
London WC2A 1AT(GB)

⑷ A method for stripping a photo resist on an aluminium alloy.

⑸ An interconnection pattern made of aluminum alloy, such as Al-Cu, on a semiconductor IC is dry etched in an etching gas. When an etching gas containing chlorine is used, residual chlorine on the substrate is difficult to remove, and causes corrosion of the patterned aluminum alloy layer. According to the present invention, the photo resist stripping process following the etching process is carried out by a downstream stripping process using a conventional etching gas, such as $CF_4 + O_2$, at room temperature, and, before the resist-stripped substrate is exposed to the atmosphere, the substrate is heated in a vacuum at higher than 100°C, thus the residual chlorine component is removed. The heating process can be carried out concurrently during the resist stripping process. By this means corrosion of the aluminum alloy interconnection is prevented.

EP 0 247 603 A3

⑩



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 247 603
A2

⑫

EUROPEAN PATENT APPLICATION

⑲ Application number: 87107743.4

⑳ Int. Cl. 4: H01L 21/31, G03F 7/26

㉑ Date of filing: 27.05.87

㉒ Priority: 29.05.86 JP 124123/86

㉓ Date of publication of application:
02.12.87 Bulletin 87/49

㉔ Designated Contracting States:
DE FR GB

DOD

㉕ Applicant: FUJITSU LIMITED
1015, Kamikodanaka Nakahara-ku
Kawasaki-shi Kanagawa 211(JP)

㉖ Inventor: Nakamura, Moritaka c/o FUJITSU
LIMITED
Pat. Dep. Kosugi Fujitsu Bldg 1812-10
Shimonumabe
Nakahara-ku Kawasaki-shi Kanagawa 211(JP)

㉗ Representative: Greenstreet, Cyril Henry et al
Haseltine Lake & Co. Hazlitt House 28
Southampton Buildings Chancery Lane
London WC2A 1AT(GB)

㉘ A method for stripping a photo resist on an aluminium alloy.

㉙ An interconnection pattern made of aluminum alloy, such as Al-Cu, on a semiconductor IC is dry etched in an etching gas. When an etching gas containing chlorine is used, residual chlorine on the substrate is difficult to remove, and causes corrosion of the patterned aluminum alloy layer. According to the present invention, the photo resist stripping process following the etching process is carried out by a downstream stripping process using a conventional etching gas, such as $CF_4 + O_2$, at room temperature, and, before the resist-stripped substrate is exposed to the atmosphere, the substrate is heated in a vacuum at higher than $100^\circ C$, thus the residual chlorine component is removed. The heating process can be carried out concurrently during the resist stripping process. By this means corrosion of the aluminum alloy interconnection is prevented.

EP 0 247 603 A2

A method for stripping a photo resist on an aluminum alloy.

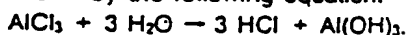
This invention relates to a method for stripping a photo resist coated on a layer of an aluminum alloy, such as aluminum-copper, formed on a semiconductor substrate.

Aluminum or aluminum-silicon alloy containing several percent of silicon has been generally used for an interconnection layer on a semiconductor device. However, it is also well known that the interconnection layer may be broken by electromigration, particularly in a semiconductor device where a very fine interconnection is required, such as 4 μm for a high speed ECL (Emitter Coupled Logic) or 1 μm for MOS (Metal Oxide Semiconductor), to achieve a greater density of integration, and a correspondingly higher density of the current flowing therethrough is required. In order to prevent this electromigration of the interconnection layer, an aluminum-copper alloy containing 2 to 4% of copper has come to be used, particularly where a high current-density is handled as in a bipolar device or a high-speed logic circuit. However, the aluminum-copper alloy suffers from problems due to residual chlorine therein.

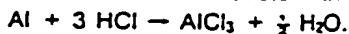
When an aluminum or aluminum alloy layer is plasma dry-etched by chlorinated gases, such as a mixture of chlorine (referred to hereinafter as Cl_2) with silicon tetrachloride (SiCl_4) or boron trichloride (BCl_3), the residual chlorine problem arises as follows:



where Cl^* denotes a chlorine radical produced in the plasma, and \uparrow denotes sublimation. The aluminum, Al, reacts with Cl^* to produce AlCl_3 or Al_2Cl_6 , which then sublimates, and the aluminum continues to be etched in this way. When the etch-processed substrate is brought out into the open air, the AlCl_3 , etc., which has sublimated and deposited on a surface of the side wall of the aluminum layer or on a photo resist reacts with atmospheric water, because the AlCl_3 is deliquescent. Hydrochloric acid (HCl) is thus produced thereon as shown by the following equation:



The HCl then reacts with the Al to produce AlCl_3 again as follows:



Thus, the reactions are continued repeatedly. In other words, the corrosion of the aluminum layer continues indefinitely. In order to prevent this corrosion, one or more of the following procedures is or are carried out for aluminum, aluminum-titanium (Al-Ti) alloy or aluminum-silicon (Al-Si) alloy, after the dry etching process:

(1) Stripping the photo resist without exposing the substrate to the open air so as to prevent the chlorine deposit on the substrate from reacting with the water content in the open air.

(2) Drying the substrate with a hot nitrogen gas blast at up to 100 to 200°C, and then washing it with water so as to remove the residual chlorine.

(3) Washing the substrate with water, and then baking it in an oxygen atmosphere at approximately 350°C so as to remove the residual chlorine.

(4) Plasma-processing the substrate in a fluorinated gas, such as CF_4 , SF_6 or CHF_3 , so as to replace the residual chlorine atoms by the fluorine atoms produced in the plasma. A stable aluminum fluoride (AlF_3 or AlF_2) is thus formed over the aluminum surface to prevent the chlorine component from reacting with water contained in the air.

(5) Plasma-processing the substrate in hydrogen gas, which reacts with the residual chlorine component to produce hydrogen chloride.

By the application of the above-mentioned procedures the residual chlorine component on the substrate made of the above-mentioned aluminum or aluminum alloys can be removed, and thus the corrosion can be prevented. However, when an aluminum alloy, such as aluminum-copper (Al-Cu) or aluminum-copper-silicon (Al-Cu-Si) is etched, its chlorine component remains in the form of Cu_2Cl_2 or a mixture of Cu, Cl, Al and carbon from the photo resist, which are difficult to remove as they have much higher sublimation temperatures than aluminum chloride, and may therefore cause corrosion even after the above-described chlorine-removal processing is carried out.

To overcome the above-mentioned problems an improved method of removing the residual chlorine is desirable.

It is an object of the invention to provide a method that may be used to form a pattern of an aluminum alloy on a semiconductor substrate without corrosion problems caused by residual chlorine on the substrate.

According to the invention, a method for etching an aluminum alloy pattern on a semiconductor substrate comprises the steps of:

forming a layer of aluminum alloy on a semiconductor substrate having an insulation layer thereon;

forming a resist pattern on said aluminum alloy layer;

5 etching an exposed portion of said aluminum alloy layer by the use of said resist pattern as a mask, whereby said aluminum alloy layer is patterned;

stripping said resist pattern in an atmosphere containing a reactive species; and

heating the substrate in a vacuum at a temperature higher than 100°C, whereby residual etching agent on the substrate is removed, said heating step being carried out concurrently with said stripping step or after

10 said stripping step.

In an embodiment of the invention, the method includes the steps of: forming a layer of aluminum-copper alloy on a semiconductor substrate; forming a resist pattern on said alloy layer; etching said alloy layer by the use of said resist pattern in a chlorinated gas plasma so as to form an alloy pattern; downstream stripping said resist pattern in an atmosphere containing a reactive species; and heating the

15 thus-processed substrate in a vacuum at a temperature higher than 100°C, to remove the residual chlorine component. The stripping process and the heating process may be combined; that is to say, be carried out concurrently.

The above-mentioned features and advantages of the present invention, together with other objects and advantages, which will become apparent, will be more fully described hereinafter with reference to the

20 accompanying drawings, in which like numerals refer to like parts throughout.

Figs. 1(a) to 1(d) are sectional views that schematically illustrate the main part of a semiconductor device at successive steps of a fabrication process according to the present invention.

Fig. 2 schematically illustrates a dry processing apparatus using microwave power, used for the stripping step of the present invention.

25 Referring now to Figs. 1(a) to 1(d), the fabrication steps in a preferred embodiment of the present invention are as follows:

By general fabrication methods (not shown in the Figures) a semiconductor substrate 1 is fabricated with IC devices therein and coated with an insulation film thereon, for example of PSG (phospho silicate glass). A layer 2 of an aluminum-copper alloy, for example Al-Cu(4%) up to approximately 8000Å thick is

30 formed all over the semiconductor substrate 1 by a known general method, such as sputtering, as shown in Fig. 1(a). A photo resist film is formed upon the alloy layer 2, and the resist film is patterned, as denoted by 3 in Fig. 1(b), by a known general lithography technique. The exposed portion of the alloy layer 2, i.e. the portion not masked by the photo resist pattern 3, is removed by a known general dry etching method. The dry etching may be a reactive ion etching method using as etching agent an etching gas such as a mixture

35 of chlorine (Cl_2) gas (24 sccm (standard cubic centimeter per minute)) and silicon tetrachloride (SiCl_4) gas (40 sccm). The gas pressure is reduced to approximately 0.02 Torr (2.67 Pa), and radio frequency power of 13.56 MHz, for example, and 250 W, for example, is applied thereto for 5 minutes, for example, by well known methods. The etching gas is dissociated in a glow discharge driven by the applied radio frequency power and the chlorine atoms produced are active to react with the aluminum as well as the copper of the

40 alloy. The aluminum chloride sublimates in the same manner as explained in the description of the prior art, and the copper chloride is sputtered by the energetic ion bombardment, so that the exposed portion of the alloy is etched and removed leaving the patterned layer 2', as shown in Fig. 1(c). Next, the substrate 1 is transferred to a dry processing apparatus for stripping the patterned photo resist 3, passing through a vacuum system or an inert gas purged system, in order to avoid being exposed to the atmosphere. If the

45 substrate is exposed to the atmosphere, the residual chlorine on the substrate reacts with water contained in the air and corrodes the alloy, as explained in the prior art.

The patterned photo resist 3 on the patterned alloy layer 2' is then stripped by a known downstream etching method. A stripping apparatus using microwave power, which is preferably employed in this stripping step, and is also called a downstream ashing or an after-glow ashing, will be described in detail

50 later. As a reaction gas in the dry etching, a mixture of a CF_4 gas (100 sccm) and oxygen (O_2) gas (1500 sccm), for example, is used at approximately 1 Torr (1.33×10^2 Pa), and microwave power of 2.45 GHz and 1 KW is applied thereto for 2 minutes, for example, while the substrate is kept at room temperature, such as 30°C. After finishing this stripping process, the substrate is heated so that the residual chlorine component is baked out. In the apparatus shown in Fig. 2 the heating is effected by the electric heater 31 built in the

55 stage 25 to approximately 300°C for 2 minutes for example while the apparatus is pumped out to 0.2-0.3

Torr ($0.27-0.4 \times 10^2$ Pa). After the substrate is cooled enough, the substrate is brought out of the apparatus, thus the processes of the invention are all finished. This method will be referred to as method I. It is also possible to heat the substrate on a separate heating stage from the stripping stage 25 in the vacuum chamber in order to save the cycle time for heating/cooling the massive stage.

The last baking process of method I may be combined with the stripping process. In other words, these two processes can be carried out concurrently. In this case, the stripping process is carried out while the substrate 1 is heated to 200 to 300°C by an electric heater 31 mounted in the stage 25. This method will be referred to as method II.

When the stripping and baking processes are combined as in method II, the etching gas may be a mixture of nitrogen (N_2) gas (100 sccm) and oxygen (O_2) gas (1500 sccm) at approximately 1 Torr (1.33×10^2 Pa), and the substrate may be heated at 200 to 300°C. This method will be referred to as method III.

In these methods, the combination of the heating and the downstream stripping is essential, because heating without stripping cannot remove the residual chlorine components under 400°C. Moreover, conventional plasma stripping causes a particle problem by Al_2O_3 formation.

In order to confirm the effect of the above-described methods of the present invention, the processed substrate was exposed to the atmosphere for 2 days. The alloy pattern was then optically observed to check for corrosion, and the residual chlorine atoms were measured by X-ray fluorescence spectroscopy. The check results are set out in the following table, in which

(a) shows the temperature of the substrate during the heating, in °C,

(b) shows existence of the corrosion found by optical observation using a microscope of magnification $\times 1000$, and

(c) shows the amount of residual chlorine atoms in units of cps (counts per second), where 10-cps corresponds to 1.64×10^4 atoms per cm^2 .

Method	I	II	II	II	II	II	III
(a)	300	30	70	110	150	200	300
(b)	no	yes	yes	no	no	no	no
(c)	8.1	141.1	122.2	21.4	11.6	9.5	8.3

As seen in the Table, when the substrate is heated at above 100°C, the residual chlorine is evidently reduced and no corrosion is observed. The amount of residual chlorine is reduced as the heating temperature is raised, but on the other hand, if the temperature exceeds 300°C, the aluminum is affected: for example hillocks are formed on the surface of the aluminum. Therefore, the temperature must be lower than 400°C, and preferably be chosen between 250 and 300°C.

An embodiment of the dry etching apparatus for stripping the photo resist will now be described in detail, with reference to Fig. 2. The apparatus employs microwave power for producing reactive species as etching agent. The substrate 1 is loaded on the stage 25 in a reaction chamber 30. In the stage 25, an electric heater 31 and a thermometer (not shown in the Figure) are mounted to heat the substrate when required. The chamber 30 is evacuated through gas outlets 26 by conventional evacuation equipment, which is not shown in the Figure. An etching gas is introduced into the chamber 30 through the gas inlet 27. By balancing the gas evacuation and gas introduction, the gas pressure within the chamber 30 is controlled to obtain the required gas pressure. A microwave-passing window 23 made of an insulating material, such as quartz or alumina, is installed perpendicularly to the electric field in the wave guide 21 and also seals the vacuum of the chamber 30. A metal shield plate 28 having many small holes therein shields the microwaves from the reaction chamber 30, so that a plasma generation chamber 29 is formed between the microwave-passing window 23 and the shield plate 28. Microwave power 22 is fed through the wave guide 21 and through the microwave-passing window 23 into the plasma generation chamber 29. In the plasma generation chamber 29, the etching gas is made into plasma by the excitation by the microwave power. A reactive species, such as oxygen atoms, produced in the plasma comes out through the holes of the shield plate 28 and flows directly down on to the substrate 1, i.e. efficiently, because the shield plate is located close to the substrate 1. This reactive species is very reactive with the photo resist on the substrate, but does not harm the substrate by an ionic bombardment as in the plasma etching because the species coming out of the holes of the shield plate 28 is not ionic and no other ionic gas comes out at all. Therefore, this type of apparatus is advantageously employed for stripping the photo resist.

Although aluminum-copper alloy is referred to in the above-described embodiment as the material to be processed, the present invention is also effective for other alloys such as AlCuSi and AlSiTiCu.

Although a mixture of Cl_2 and SiCl_4 is referred to as an etching gas for etching the alloy in the above-described embodiment, other gases of chlorine family, such as BCl_3 , CCl_4 and CHCl_3 , can be also used therein, as is well known.

Although a dry etching apparatus using a radio frequency of 13.56 MHz is referred to in the above-described embodiment for etching the alloy, other types of dry etching apparatus, for example using a radio frequency of 400 KHz, can also be used, as is well known.

Although a mixture of CF_4 , N_2 and O_2 is referred to as an etching gas for stripping the photo resist in the above-described embodiment, other fluorinated gases, such as CHF_3 , C_2F_6 , SF_6 , NF_3 or CBrF_3 , can be also used, singly or mixed, in place of CF_4 , and other nitrogen-containing gases, such as N_2O or NO_2 , can be also used in place of N_2 , as is well known.

Although a dry etching apparatus using a microwave frequency of 2.45 GHz is referred to in the above-described embodiment for stripping the photo resist, other types of dry etching apparatus, e.g. using a radio frequency of 13.56 MHz, can also be used, as is well known.

The many features and advantages of the invention are apparent from the detailed specification. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention as claimed.

Claims

1. A method for etching an aluminum alloy pattern on a semiconductor substrate, comprising the steps of:

forming a layer of aluminum alloy on a semiconductor substrate having an insulation layer thereon;
forming a resist pattern on said aluminum alloy layer;
etching an exposed portion of said aluminum alloy layer by the use of said resist pattern as a mask, whereby said aluminum alloy layer is patterned;
stripping said resist pattern in an atmosphere containing a reactive species; and heating the substrate in a vacuum at a temperature higher than 100°C , whereby residual etching agent on the substrate is removed, said heating step being carried out concurrently with said stripping step or after said stripping step.

2. A method according to claim 1 wherein said etching is carried out by a dry etching method.

3. A method according to claim 2 wherein said dry etching is carried out by the use of a gas containing chlorine.

4. A method according to claim 3 wherein said gas is chosen from the group of chlorine gas, silicon tetrachloride gas, boron trichloride gas, and carbon tetrachloride gas.

5. A method according to any preceding claim wherein the temperature in said heating step is lower than approximately 400°C .

6. A method according to any preceding claim, wherein said reactive species are produced from a mixture of a fluorinated gas and oxygen gas.

7. A method according to any one of claims 1 to 5, wherein said reactive species are produced from a mixture of a nitrogen-containing gas and oxygen gas.

8. A method according to any preceding claim, wherein said reactive species is produced by excitation by microwave power of approximately 2.45 GHz.

9. A method according to any preceding claim wherein said aluminum alloy is an aluminum-copper alloy.

FIG. 1(a)

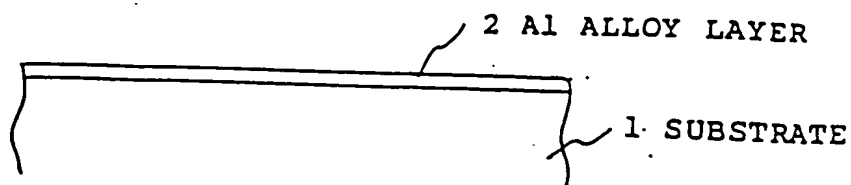


FIG. 1(b)

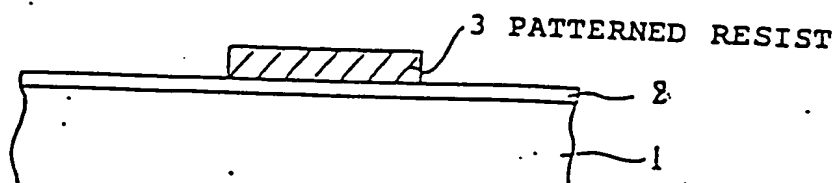


FIG. 1(c)

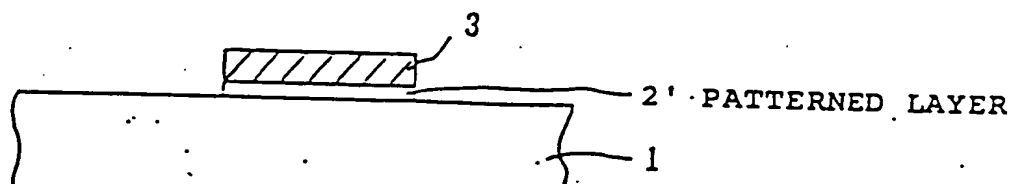
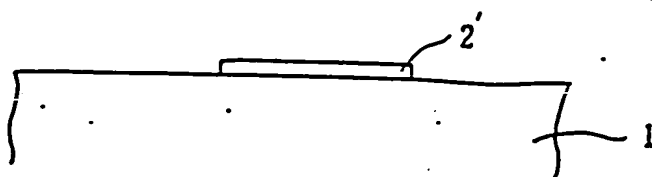


FIG. 1(d)



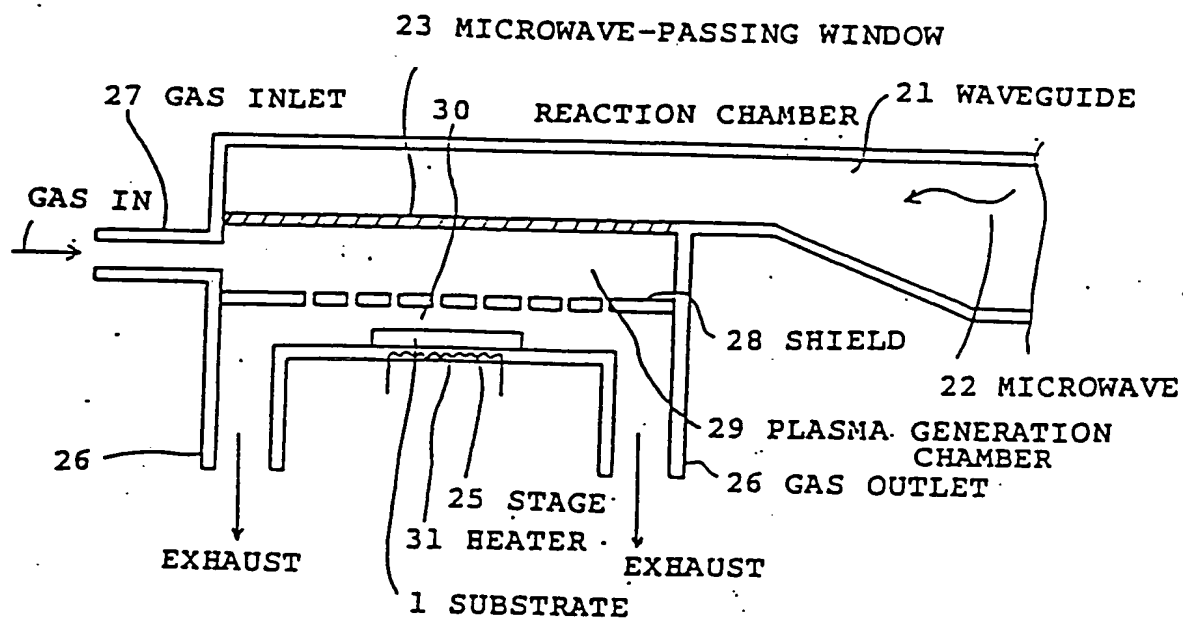


FIG. 2



EP 87 10 7743

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	PATENT ABSTRACTS OF JAPAN, vol. 5, no. 117 (E-67)[789], 28th July 1981; & JP-A-56 55 050 (FUJITSU K.K.) 15-05-1981 * Whole abstract *	1-4,8,9	H 01 L 21/31 . G 03 F 7/26
Y	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 81 (E-238)[1518], 13th April 1984; & JP-A-59 3927 (FUJITSU K.K.) 10-01-1984 * Whole abstract *	1-4,8,9	
X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 47 (E-299)[1770], 27th February 1985; & JP-A-59 186 326 (HITACHI SEISAKUSHO K.K.) 23-10-1984 * Whole abstract *	1,2	
A	EP-A-0 010 138 (IBM) * Abstract; claims *	1-5,9	
A	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 21, no. 6, November 1978, page 2315, New York, US; G.T. CHIU et al.: "Plasma removal of residue following reactive ion etching of aluminum and aluminum alloys" * Whole document *	1-3,6,9	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) H 01 L
A	US-A-4 370 195 (RCA) * Abstract; claims *	1-4,9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-03-1988	Examiner GORI P.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	